

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C09D 11/00	A1	(11) International Publication Number: WO 98/27170 (43) International Publication Date: 25 June 1998 (25.06.98)
(21) International Application Number: PCT/GB97/03404 (22) International Filing Date: 10 December 1997 (10.12.97) (30) Priority Data: 08/770,753 19 December 1996 (19.12.96) US (71) Applicant: THE GENERAL ELECTRIC COMPANY, PLC [GB/GB]; 1 Stanhope Gate, London, W1A 1EH (GB). (72) Inventor: ZHU, Linfang; 338 Meadow Green Drive, Naperville, IL 60565 (US). (74) Agent: MCGOWAN, Nigel, George; GEC Patent Dept., Waterhouse Lane, Chelmsford, Essex CM1 2QX (GB).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: A JET INK COMPOSITION (57) Abstract <p>Disclosed is a jet ink composition suitable for printing marks on metal, glass, plastics, rubber, or paper comprising an ink carrier, a fluorescent colorant, a cellulosic binder resin, and a tetraalkyl ammonium or phosphonium salt. The jet printed marks do not blush, bleed, or fade, as a result of exposure to steam, or hot and cold water. Also disclosed is an improved process of jet printing on substrates comprising printing with the disclosed jet ink composition.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australja	GA	Gabon	LV	Larvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

5

A JET INK COMPOSITION

The present invention generally relates to ink jet printing fluorescent ink compositions, and particularly to ink jet printing fluorescent ink compositions whose marks resist blushing, bleeding, or fading as a result of exposure to water.

Ink jet printing is a well-known technique by which printing is accomplished without contact between the printing device and the substrate on which the printed characters are deposited. Briefly described, ink jet printing involves the technique of projecting a stream of ink droplets to a surface and controlling the direction of the stream electronically so that the droplets are caused to form the desired printed image on that surface. This technique of noncontact printing is particularly well suited for application of characters onto irregularly shaped surfaces, including, for example, the bottom of glass, metal, or plastic containers, used for holding cosmetic, pharmaceutical, liquor, and health care products.

Reviews of various aspects of ink jet printing can be found in these publications: Kuhn et al., *Scientific American*, April, 1979, 162-178; and Keeling, *Phys. Technol.*, 12(5), 196-303 (1981). Various ink jet apparatuses are described in the following U.S. Patents: 3,060,429, 3,298,030, 3,373,437, 3,416,153, and 3,673,601.

In general, an ink jet ink composition must meet certain rigid requirements to be useful in ink jet printing operations. These relate to viscosity, resistivity, solubility, compatibility of components and wettability of the substrate. Further, the ink must be

quick-drying, smear resistant, and be capable of passing
5 through the ink jet nozzle without clogging, and permit
rapid cleanup of the machine components with minimum
effort.

The marking of articles such as bank checks,
envelopes, certificates, and the like, as well as food
10 containers such as metal, plastic or glass containers
with identification marks for later identification and/or
sorting is well known. Several methods have been
proposed for producing such security or identification
marks. For example, infrared readable bar codes have
15 been proposed. See, e.g., Japanese Patent Application
Kokai No. 58-45999 and U.S. Patent 5,366,252.

The methods based on infrared readable materials
have the disadvantage that the infrared absorbing bar
codes are to some extent visible to the unaided eye and
20 need to be physically concealed. The concealment of the
bar code results in covering up of a portion of the
article, thereby adversely affecting the aesthetics of
the article.

Fluorescent materials have been considered for
25 marking purposes. It is known that fluorescence is the
property of a material to emit radiation as the result of
exposure to radiation from some other source. The
emitted radiation persists only as long as the exposure
is subjected to radiation. The fluorescent radiation
30 generally has a wavelength longer than that of the
absorbed radiation.

There has been significant developmental activity in
the area of fluorescent jet inks for producing security
marks on envelopes and documents. For instance,
35 U.S. Patent 5,093,147 discloses a method for providing
intelligible marks that are virtually invisible to the
unaided eye on the surface of an article. The method
employs a jet ink containing an organic laser dye that is

poorly absorptive in the visible range of about 400 to
5 700 nm, is absorptive of radiation in the near infrared
range of at least 750 nm, and fluoresces in response to
radiation excitation in the infrared range at a
wavelength longer than that of the exciting radiation.

U.S. Patent 4,736,425 discloses a method of marking
10 fiduciary documents requiring authentication by the use
of certain fluorescent chelates. The method comprises
introducing only a part of the elements forming the
chelate onto the document to be marked and subsequently
contacting the document for authentication purpose with
15 the missing part of the elements forming the chelate to
effect the synthesis of the fluorescent chelate. The
chelate thus formed is excited by ultraviolet radiation
and the resulting fluorescence radiation is detected.

U.S. Patent 4,450,595 discloses a jet ink that can
20 be used to mark documents such as bank checks for
automatic identification. The ink contains certain
phenoxazine derivative dyes that are visible to the
unaided eye and fluoresce in the near infrared region
(650 to 800 nm) upon activation using an activating light
25 having a wavelength in the range of 550 to 700 nm. The
ink that is visible to the unaided eye is unfortunately
not suitable for many security mark applications.

Commonly owned and copending U.S. patent application
Serial No. 08/661,180, filed June 10, 1996, discloses jet
30 ink compositions suitable for marking on white or light
colored substrates such as envelopes. The ink
composition comprises a fluorescent colorant and an ink
carrier. The colorant comprises a rare earth metal and a
chelating agent. The mark produced by the ink
35 composition is completely or substantially invisible to
the unaided eye and is visible only when excited by
ultraviolet light.

Metal containers such as, for example, empty

containers used to can foods or beverages such as coffee,
5 beer, soup, and others are shipped to the fillers with
identification marks placed thereon by the container
manufacturer. At the fillers' premises, the containers
are subjected to various treatments including autoclaving
in presence of steam, and immersing the containers in
10 water. The autoclaving is carried out at temperatures as
high as 250°F for times up to 30 minutes. The immersion
testing typically is carried out by immersing the
containers in selected temperature waters ranging from
ice water to boiling water for a period ranging from
15 about 5 minutes to about 30 minutes. It has been a
problem with some of the previously known fluorescent jet
ink compositions that the marks tend to blush, bleed, or
fade as a result of one or more of these treatments.
When the mark becomes visible to the unaided eye, it is
20 said to have blushed. When the mark becomes diffuse, it
said to have bled. When the mark becomes unreadable or
poorly readable due to reduced color intensity, it is
said to have faded.

In the area of marking objects such as metals, the
25 following publications are of interest. German Patent DE
3529798 reportedly discloses a jet ink for placing on
metals, plastics, paper, or glass identification marks
that are invisible to the naked eye consisting of an
alcohol solvent, a fluorescent substance that is soluble
30 in a water/ethanol mixture, a water-soluble polyacrylate,
and optionally a water-soluble cellulose ester and
diethanolamine.

German Patent DE 4013456 reportedly discloses a jet
ink containing an organic solvent, a fluorescent
35 dyestuff, a polyamic acid or polyimide binder resin, and
conductive salts. The ink is said to adhere well to
glass, ceramic, and copper.

Commonly owned and copending U.S. patent application

Serial No. 08/686,191, filed July 26, 1996, discloses a
5 jet ink composition suitable for producing blush
resistant marks that are invisible to the unaided eye and
are visible only when excited by an exciting radiation
comprising a solvent, a fluorescent colorant, a binder
resin, and a plasticizer having a vapor pressure of about
10 15 mm Hg or less at 240 °C.

The foregoing indicates that there exists a need for
a jet ink composition comprising a fluorescent colorant
suitable for printing identification marks on metals,
glass, ceramics, and plastics.

15 Thus, there exists a need for a jet ink composition
suitable for printing on substrates, particularly metal
containers, marks that resist blushing. There also
exists a need for a jet ink composition suitable for
printing on substrates, particularly metal containers,
20 marks that resist bleeding. There also exists a need for
a jet ink composition suitable for printing on
substrates, particularly metal containers, marks that
resist fading.

The present invention provides a jet ink
25 composition comprising a fluorescent colorant suitable
for printing identification marks on metals, glass,
plastic, ceramics, or paper.

The jet ink composition of the present invention
comprises an ink carrier, a fluorescent colorant, a
30 cellulosic binder resin, and a tetraalkyl ammonium or
phosphonium salt.

The marks printed using the inventive jet ink
composition have at least one, and preferably more than
one, advantage. These advantages are blush resistance,
35 bleed resistance, and fade resistance.

The present invention further provides an improved
process of jet printing on metal, glass, plastic, rubber,
or paper substrates. The improvement comprises

projecting a stream of ink droplets of a jet ink
5 composition to the surface of the substrates and
controlling the direction of the stream electronically so
that the droplets are caused to form the desired marks on
the surface.

The present invention provides jet ink compositions
10 suitable for printing marks that are invisible to the
unaided eye and are visible only when excited by an
exciting radiation.

The present invention further provides a jet ink
composition suitable for producing blush resistant marks
15 that are invisible to the unaided eye and are visible
only when excited by an exciting radiation.

The present invention further provides a jet ink
composition suitable for producing bleed resistant marks
that are invisible to the unaided eye and are visible
20 only when excited by an exciting radiation.

The present invention further provides a jet ink
composition suitable for producing fade resistant marks
that are invisible to the unaided eye and are visible
only when excited by an exciting radiation.

25 In general, the jet ink composition of the present
invention exhibit the following characteristics for use
in ink jet printing systems: (1) a Brookfield viscosity
of from about 1.6 to about 7.0 centipoises (cps) at 25
°C; (2) an electrical resistivity of from about 20 to
30 about 2000 ohm-cm; and (3) a sonic velocity of from about
1100 to about 1700 meters/second.

A detailed discussion of the various components and
a method of preparation of the inventive jet ink
composition is set forth below.

FLUORESCENT COLORANTS

5 Any suitable fluorescent colorant that is substantially or completely invisible to the unaided eye can be used in the preparation of the inventive ink composition. The fluorescent colorant absorbs outside the visible range, and fluoresces at a wavelength longer
10 than the absorption wavelength. Preferably, the fluorescent colorant absorbs in the wavelength region of from about 275 nm to about 400 nm and emits in the wavelength region of from about 420 nm to about 520 nm. A fluorescent colorant that emits a blue line is further
15 preferred.

An example of a suitable fluorescent colorant is 2,2'-(2,5-thiophenediyl)-bis(5-tert-butylbenzoxazole), which is available as UVITEX OB from Ciba-Geigy Corp. in Hawthorne, New York. UVITEX OB is a yellow crystalline
20 powder having a melting point of 197-203 °C. It has good lightfastness, excellent resistance to heat, and high chemical stability. UVITEX OB can be heated for 8 hours at 300 °C in a nitrogen atmosphere without decomposition. The colorant also can be heated for the same period at
25 200°C in air without decomposition. UVITEX OB has an absorption maximum at 375 nm (extinction coefficient 1,200 at 1%, 1 cm) and a fluorescence maximum at 435 nm when measured in ethanol solution. The colorant produces a blue fluorescence. UVITEX OB is known to be useful as
30 an optical brightener in plastics.

Examples of other optical brighteners can be found in Kirk-Othmer Encyclopedia of Chemical Technology, 4, "Fluorescent Brighteners", pp. 213-225 (1978), and include the stilbene derivatives such as 4,4'-
35 bis(triazin-2-ylamino)stilbene-2,2'-disulfonic acid derivatives wherein the triazinyl groups are substituted with suitable substituents, including substituents such

as anilino, sulfanilic acid, metanilic acid, methylamino,
5 N-methyl-N-hydroxyethylamino, bis(hydroxyethylamino),
morpholino, diethylamino, and the like; mono(azol-2-
yl)stilbenes such as 2-(stilben-4-yl)naphthotriazoles and
2-(4-phenylstilben-4-yl)benzoxazoles; bis(azol-2-
yl)stilbenes such as 4,4'-bis(triazol-2-yl)stilbene-2,2'-
10 disulfonic acids; styryl derivatives of benzene and
biphenyl such as 1,4-bis(styryl)benzenes and 4,4'
bis(styryl)biphenyls; pyrazolines such as 1,3-diphenyl-2-
pyrazolines; bis(benzazol-2-yl) derivatives having as
phenyl ring substituents alkyl, COO-alkyl, and SO₂-alkyl;
15 bis(benzoxazol-2-yl) derivatives; bis(benzimidazol-2-yl)
derivatives such as 2-(benzofuran-2-yl)benzimidazoles;
coumarins such as 7-hydroxy and 7-(substituted
amino)coumarins, 4-methyl-7-amino-coumarin derivatives,
esculetin, β -methylumbelliferone, 3-phenyl-7-(triazin-2-
20 ylamino)coumarins, 3-phenyl-7-aminocoumarin, 3-phenyl-7-
(azol-2-yl)coumarins, and 3,7-bis(azolyl)coumarins;
carbostyrils, naphthalimides, alkoxynaphthalimides,
derivatives of dibenzothiophene-5,5-dioxide, pyrene
derivatives, and pyridotriazoles.

25 Coumarin type fluorescent colorants can be obtained
commercially from BASF Corp. in Holland, Michigan. Thus,
coumarin is sold as CALCOFLUOR WHITE LD or Fluorescent
Brightener 130, which has an absorption maximum at 367.8
nm and an emission maximum at 450 nm. Aminocoumarin is
30 sold as CALCOFLUOR WHITE RWP Conc. or RW Solution. The
aminocoumarins have an absorption maximum at 374.5 nm and
an emission maximum at 450 nm.

Other examples of fluorescent colorants include rare
earth metal chelates, and preferably, lanthanide
35 chelates. Examples of lanthanide chelates include those
formed by the chelation of organic ligands such as
acetylacetone, benzoylacetone, dibenzoylmethane, and
salicylic acid with lanthanide ions such as neodymium,

europium, samarium, dysprosium, and terbium ions.

- 5 Examples of such complexes include europium acetylacetonate, samarium acetylacetonate, neodymium benzoylacetonate, terbium salicylate, and dysprosium benzoylacetonate. The aforesaid chelates can be prepared by any suitable method known to those of ordinary skill
- 10 in the art. For example, a ligand such as acetylacetone can be reacted under suitable conditions with a rare earth metal halide such as europium trichloride to produce the rare earth metal chelate. For additional details, see U.S. Patent 4,736,425. The above chelates
- 15 absorb ultraviolet radiation and fluoresce in the visible range. The acetylacetonate of europium fluoresces with an emission line in the red region and this is particularly suitable for printing on white or light colored substrates. Examples of commercially
- 20 available rare earth chelate fluorescent colorants suitable for use in the ink composition of the present invention include, but are not limited to, the rare earth metal chelates sold as LUMILUX C™ pigments by Hoechst-Celanese Corp. in Reidel-de Haen, Germany.
- 25 The LUMILUX C rare earth metal organic chelates have a melting point of from about 130 °C to about 160 °C and a bulk density of from about 500 kg/m³ to about 1100 kg/m³. Examples of organic LUMILUX C pigments include Red CD 316, Red CD 331, Red CD 332, Red CD 335, and Red CD
- 30 339, which are yellowish when unexcited and fluoresce in the orange-red region when excited by ultraviolet radiation. These pigments are soluble in organic solvents. Red CD 331, a preferred pigment and a derivative of europium-acetonate, is a yellowish powder
- 35 having an emission peak at 612 nm, a melting point in the range of 153-155 °C, and a density of 600 kg/m³. Red CD 331 is soluble in acetone, ethylacetate, ethanol, xylene, dichloromethane, dimethylformamide, n-hexane, and

dibutylphthalate. Red 316 is a rare earth
5 acetylacetonate. Red CD 332, a rare earth biketonate,
has a melting of 135-138 °C and a density of 500 kg/m³.
Red CD 335, an europium chelate, has a melting point of
133 °C and a density of 1030 kg/m³.

Additional examples of suitable LUMILUX pigments
10 include Red CD 105, Red CD 106, Red CD 120, and Red CD
131. These are inorganic pigments. Red CD 105 is white
when unexcited, fluoresces in the orange-red region when
excited by ultraviolet radiation, and has a median
particle size of 7 microns. Red CD 106 is white when
15 unexcited, fluoresces in the orange-red region when
excited by ultraviolet radiation, and has a median
particle size of 6 microns. Red CD 120 is white when
unexcited, fluoresces in the red region when excited by
ultraviolet radiation, and has a median particle size of
20 2.7 microns. Red CD 131 is white when unexcited,
fluoresces in the red region when excited by ultraviolet
radiation, and has a median particle size of 6.5 microns.
It is preferred that the particle size of the aforesaid
pigments is further reduced by suitable means including
25 grinding and crushing for use in the preparation of the
jet ink composition.

Examples of other fluorescent colorants include the
porphyrin type dyes described in U.S. Patent 5,256,193.
These include, e.g., the tetra- chloride, bromide,
30 tosylate, triflate, perchlorate, acetate, and
fluoroborate salts of 5,10,15,20-tetrakis-(1-methyl-4-
pyridyl)-21H,23H-porphine, 5,10,15,20-tetrakis-(1-
hydroxymethyl-4-pyridyl)-21H,23H-porphine, 5,10,15,20-
tetrakis-[1-(2-hydroxyethyl)-4-pyridyl]-21H,23H-porphine,
35 5,10,15,20-tetrakis-[1-(3-hydroxypropyl)-4-pyridyl]-
21H,23H-porphine, 5,10,15,20-tetrakis-[1-(2-
hydroxyethoxyethyl)-4-pyridyl]-21H,23H-porphine, and
5,10,15,20-tetrakis-[4-(trimethylammonio)phenyl]-21H,23H-

porphine. These colorants are excitable in the 380-500
5 nm range, and fluoresce in the 600-800 nm range.

Any suitable amount of the colorant can be used to
prepare the jet ink composition of the present invention.
If the ultraviolet absorptivity or the fluorescent
emission intensity is high, then a small amount of the
10 colorant is sufficient. If the ultraviolet absorptivity
or the fluorescent emission intensity is low, then the
amount of the colorant used should be increased. The
colorant is used preferably in an amount of from about
0.01% by weight to about 1% by weight of the jet ink
15 composition, and more preferably in an amount of from
about 0.1% by weight to about 0.5% by weight of the jet
ink composition.

INK CARRIER

20 The jet ink composition of the present invention
comprises one or more solvents as the ink carrier. Any
suitable solvent can be used in the preparation of the
inventive jet ink composition, and preferably one or more
organic solvents are employed. It is further preferred
25 that the solvent evaporates rapidly under the printing
conditions and without leaving behind a solvent residue.
Organic solvents suitable for the preparation of the jet
ink composition of the instant invention include ketones
such as acetone, methyl ethyl ketone, diethyl ketone,
30 cyclohexanone, and the like, esters such ethyl acetate,
propyl acetate, butyl acetate, amylacetate, and the like,
alcohols such methanol, ethanol, n-propanol, isopropanol,
n-butanol, i-butanol, t-butanol, n-pentanol, n-hexanol,
and the like. If desired, a mixture of solvents may be
35 used.

Any suitable amount of the ink carrier can be used
in the preparation of the jet ink composition of the
present invention. The ink carrier is typically present

in an amount of from about 30% to about 80% by weight,
5 and preferably in an amount of from about 60% to about
75% by weight of the jet ink composition.

BINDER RESINS

The jet ink composition of the present invention
10 comprises at least one binder resin which forms a film on
the colorant. The binder resin also serves to improve the
adhesion of the colorant and other ingredients to the
printed surface. The binder resin is preferably
colorless and thus does not impart visibility to the
15 marks. Any suitable binder resin can be employed, and
preferably a good film former is employed. A good film
former rapidly forms a tough durable film as the result
of the evaporation of the solvent.

It is preferred that the binder resin, or the main
20 binder resin when a mixture of binder resins is employed,
has a melting point or softening point above about 100
°C. It is further preferred that the melting or
softening point is about 120 °C or higher, and it is even
further preferred that the melting or softening point is
25 in the range of from about 120 °C to about 200 °C. In
certain embodiments of the present invention, the melting
point or softening point of the binder resin can be about
150 °C or higher, especially for producing a mark that
can survive the autoclaving treatment.

30 It is further preferred that the binder resin has
low water absorption, preferably below about 3% by weight
of the binder resin, and more preferably below about 1%
by weight of the binder resin. It is also preferred that
the binder resin has a low acid number, preferably below
35 about 50, and more preferably below about 10. It is
further preferred that the binder resin is soluble in
common organic solvents such as ketones, alcohols, or
esters.

Examples of suitable binder resins include

5 cellulosic resins such as nitrocellulose, cellulose acetate, cellulose acetate butyrate, and cellulose acetate propionate. Several grades of nitrocellulose, a preferred binder resin, are available commercially, e.g., from Hercules, Inc. in Wilmington, DE. These grades vary

10 in nitrogen content and viscosity. The nitrogen content of the nitrocellulose resin is preferably in an amount of from about 11% by weight to about 13% by weight, and more preferably in an amount of from about 11.8% by weight to about 12.2% by weight of the resin. Hercules' RSTM type

15 nitrocellulose has an average nitrogen content of 12% by weight and is available in a large number of viscosity grades, from 10 centipoises to about 2,000 seconds, measured on a 12.2% by weight solution in toluene. The nitrocellulose resin having low viscosities, e.g., a

20 viscosity of about 10-15 cps, is particularly preferred.

The RS type nitrocellulose resins have a softening point range of 155-220 °C, and the moisture absorption of unplasticized clear film at 21 °C in 24 hours in 80% relative humidity is 1% by weight.

25 Cellulose acetate propionate (CAP) and cellulose acetate butyrate (CAB) can be obtained from Eastman Chemical, Kingsport, Tennessee. CAB-553-0.4 has a glass transition temperature of 136 °C and a melting point of 150 °C, and CAP-504-0.2 has a glass transition

30 temperature of 159 °C and a melting point of 190 °C.

The binder resin can be present in the jet ink composition in any suitable amount. It is preferably present in an amount of from about 5% by weight to about 15% by weight of the jet ink composition, and more

35 preferably in an amount of from about 10% by weight of the jet ink composition.

Certain embodiments of the jet ink composition include, in addition to the cellulosic resin, a silicone

resin. For example, it has been found that uncoated
5 aluminum substrates can be printed advantageously using
jet ink compositions containing nitrocellulose and
silicone resins.

Any suitable silicone resin can be used, linear,
branched or crosslinked, preferably those having a weight
10 average molecular weight of from about 1000 to about
10,000, more preferably those having a weight average
molecular weight of from about 2000 to about 8000, and
even more preferably those having a weight average
molecular weight of from about 2000 to about 4000. A
15 particularly preferred silicone resin is the DOW CORNING™
6-2230 resin. The DC-6-2330 resin has a silanol content
of 5% by weight of the resin, a weight average molecular
weight of 2000-4000, and a degree of crosslinking of 1.2
on a scale where 1.0 is completely crosslinked and 2.0 is
20 fully linear.

The silicone resin can be present in the jet ink
composition in any suitable amount. It is typically
present in an amount of up to about 5% by weight of the
jet ink composition, preferably in an amount of from
25 about 1% by weight to about 3% by weight of the jet ink
composition.

SURFACTANT

The jet ink composition may further contain a
30 surfactant, which may be anionic, cationic, nonionic, or
amphoteric. Examples of anionic surfactants include
alkylbenzene sulfonates such as dodecylbenzene sulfonate,
alkylnaphthyl sulfonates such as butyl or nonyl naphthyl
sulfonate, dialkyl sulfosuccinates such as diamyl
35 sulfosuccinate, alcohol sulfates such as sodium lauryl
sulfate, and perfluorinated carboxylic acids such as
perfluorodecanoic acid and perfluorododecanoic acid.
Nonionic surfactants include the alkylesters of

polyethylene glycol, fatty acid esters of glycerol, fatty
5 acid esters of glycol, and the like, and fluorochemical
surfactants such as FC 170C, FC 430, FC 431, FC 740, FC
120, FC 248, FC 352, FC 396, FC 807, and FC 824, which
are available from 3M Co. FC 430 and FC 431 are
fluoroaliphatic polymeric esters. Cationic surfactants
10 include alkylamines, amine oxides, amine ethoxylates,
alkyl hydroxyalkyl imidazolines, quaternary ammonium
salts, and amphoteric surfactants include the
alkylbetaines, the amidopropylbetaines, and the like.
The surfactant may be present in the jet ink composition
15 in any suitable amount. When a surfactant is used, it is
typically used in an amount of from about 0.01% to about
1% by weight of the jet ink composition, and preferably
in an amount of about 0.1% by weight of the jet ink
composition..

20

PLASTICIZER

The jet ink composition of the present invention
includes one or more plasticizers. It is believed that
the plasticizer may also contribute to the improved
25 properties of the marks, particularly the blush
resistance. It is also believed that the hydrophobic
plasticizer prevents or retards the diffusion of water,
especially hot water, into the film formed by the binder
resin.

30 Any suitable hydrophobic plasticizer can be used.
Examples of suitable plasticizers include trialkyl
phosphates, wherein the alkyl group can be branched or
linear and have about 1 to about 10 carbon atoms,
preferably about 3 to about 5 carbon atoms. A particular
35 example of a suitable plasticizer is tributyl phosphate,
which also acts as a flame retardant.

The plasticizer can be present in the jet ink
composition in any suitable amount. It is typically

present in an amount of up to about 5% by weight, and
5 preferably in an amount of from about 1% to about 3% by
weight of the jet ink composition.

HIGH BOILING SOLVENT

The jet ink composition of the present invention may
10 further contain a high boiling solvent, preferably a
hydrophilic high boiling solvent. When the jet printed
ink dries on the substrate, due to the evaporation of the
volatile solvents, the mark can cool rapidly and absorb
moisture from the surrounding. The absorbed moisture can
15 impart a cloudy appearance to the film formed on the
colorant. It has been observed that by including a high
boiling hydrophilic solvent in the ink composition, it is
possible to reduce or eliminate the development of
cloudiness. The hydrophilic solvents have boiling points
20 preferably above 100 °C, and more preferably in the range
of from about 150 °C to about 250 °C.

Any suitable hydrophilic high boiling solvent known
to those of ordinary skill in the art can be used.
Examples of suitable high boiling solvents include
25 glycols such as ethylene glycol, propylene glycol,
glycerin, diglycerin, diethylene glycol, and the like,
glycol ethers such as ethylene glycol dimethyl ether,
ethylene glycol diethylether, cellosolve, diethylene
glycol monoethylether (Carbitol), diethylene glycol
30 dimethylether, and diethylene glycol diethylether dialkyl
sulfoxides such as dimethyl sulfoxide, and other solvents
such as sulfolane, N-methyl pyrrolidinone (NMP), and the
like. NMP is a preferred high boiling solvent.

Any suitable amount of the high boiling solvent can
35 be used, preferably in an amount of up to about 5% by
weight of the jet ink composition, and more preferably in
an amount of from about 2% by weight to about 4% by
weight of the jet ink composition.

CONDUCTIVITY AGENT

5 The jet ink composition of the present invention further contains a conductivity agent which offers the desired electrical conductivity to the jet ink composition. It has been found that hygroscopic electrolytes tend to absorb water into the mark when
10 exposed to high humidity or water. It is believed that the absorbed water forms micro-droplets in the film on the substrate. When water is later evaporated during drying of the marks, micro-voids are formed in the film, and the micro-voids scatter light. The difference
15 between the refractive indices of the resin(s), which are generally greater than 1, and of air, which is 1, is responsible for the scattering effect. The scattering of light contributes to blushing.

It has been discovered that non-hygroscopic
20 conductivity agents are effective in reducing or eliminating blushing. Any suitable non-hygroscopic conductivity agent can be used, preferably an organic salt is used. Examples of suitable organic salts include tetraalkyl ammonium salts and tetraalkyl phosphonium
25 salts. The alkyl groups can be of any suitable number of carbon atoms, preferably about 1-10 carbon atoms, and more preferably about 2 to about 5 carbon atoms. Particular examples of preferred conductivity agents include tetraethyl or tetrabutyl ammonium or phosphonium
30 salts. The salts can contain any suitable anion. Examples of suitable anions include chloride, bromide, and p-toluenesulfonate. Thus, particular examples of non-hygroscopic conductivity agents include tetraethyl ammonium chloride, tetraethyl ammonium bromide,
35 tetrabutyl ammonium chloride, tetrabutyl ammonium bromide, tetrabutyl phosphonium chloride, tetrabutyl phosphonium bromide, and tetraethyl ammonium p-toluenesulfonate, which can be obtained from Aldrich

Chemical Co. in Milwaukee, WI.

5 Any suitable amount of the conductivity agent can be used to achieve the desired electrical conductivity. The agent is preferably present in the jet ink composition in an amount of from about 0.1% to about 2% by weight of the jet ink composition, and more preferably in an amount of
10 from about 0.4% by weight to about 1.2% by weight of the jet ink composition.

The jet ink composition of the present invention can be prepared by any suitable method known to those of ordinary skill in the art. For example, the components
15 can be sequentially added to a mixer and blended until a smooth ink composition is obtained. The ink composition can be filtered, e.g., using a 5-micron sock filter, to remove any impurities.

The following examples further illustrate the
20 present invention but, of course, should not be construed as in any way limiting its scope.

EXAMPLE 1

This Example illustrates a preferred combination of
25 the various ingredients of the jet ink composition of the present invention. IPA below stands for isopropanol.

<u>Materials</u>	<u>Preferred Range, Wt.%</u>
30 Acetone (Solvent)	about 50.0-about 95.0
Methanol (Solvent)	up to about 30.0
1-Methyl 2-Pyrrolidone (Solvent)	up to about 5.0
Nitrocellulose RS (10-15 cps, wetted with 30% IPA) (Binder)	about 5.0-to
35 about 15.0	
Silicon DC6-2230 (Binder)	up to about 5.0
Tetrabutylphosphonium Bromide (Conductive salt)	about 0.4-to about 1.2
Tributyl phosphate (Plasticizer)	about 1.0-to about 5.0
40 FC-430 (10% in acetone)	
(Surfactant)	up to about 1.0
UVITEX OB (Brightener)	about 0.1-to about 0.5

EXAMPLE 2

5 This Example illustrates an optimal combination of ingredients of the jet ink composition of the present invention illustrated in Example 1.

	<u>Materials</u>	<u>Wt. %</u>
10	Acetone	62.5
	Methanol	19.5
	1-methyl-2-pyrrolidone	3.0
	Nitrocellulose	10.0
	Silicone DC6-2230	2.0
15	Tetrabutylphosphonium bromide	0.6
	Tributylphosphate	2.0
	FC-430	0.1
	UVITEX OB	0.3
20		<u>100.0</u>

A jet ink composition was prepared using the ingredients listed above by combining and mixing them until a smooth ink composition was obtained.

EXAMPLE 3

25 This Example illustrates another preferred combination of the various ingredients that can be used to prepare a jet ink composition of the present invention.

	<u>Materials</u>	<u>Preferred Range, Wt %</u>
	Methyl ethyl ketone (Solvent)	about 30.0-to about
35	80.0	
	Methanol (Solvent)	about 10.0-to about 50.0
	1-Methyl 2-Pyrrolidone (Solvent)	up to about 5.0
	Nitrocellulose RS (10-15 cps, wetted with 30% IPA)	
40	(Binder)	about 5.0-to about 15.0
	Silicon DC6-2230 (Binder)	up to about 5.0
	Tetrabutylphosphonium Bromide (Conductive salt)	about 0.5-to about 1.5
45	Tributyl phosphate (Plasticizer)	about 1.0-to about 5.0
	FC-430 (10% in acetone)	

20

5

(Surfactant)	up to about 1.0
UVITEX OB (Brightener)	about 0.1-to about 1.0

10

EXAMPLE 4

This Example illustrates an optimal combination of ingredients of the jet ink composition of the present invention illustrated in Example 3.

15	<u>Materials</u>	<u>Wt. %</u>
	Methyl ethyl ketone	61.65
	Methanol	20.0
	1-Methyl-2-pyrrolidone	3.0
	Nitrocellulose	10.0
20	Silicone DC6-2230	2.0
	Tetrabutylphosphonium bromide	1.0
	Tributylphosphate	2.0
	FC-430	0.1
	UVITEX OB	0.25
25		<u>100.00</u>

A jet ink composition was prepared using the ingredients listed above by combining and mixing them until a smooth ink composition was obtained.

30

EXAMPLE 5

This Example illustrates another preferred combination of the various ingredients of the jet ink composition of the present invention.

35	<u>Materials</u>	<u>Preferred Range, Wt.%</u>
	Acetone (Solvent)	about 50.0-to about 95.0
	Duplicating fluid #5,	
40	anhydrous (Solvent)	up to about 30.0
	1-Methyl 2-Pyrrolidone	
	(Solvent)	up to about 5.0
	Nitrocellulose RS (10-15 cps,	
	wetted with 30% IPA)	
45	(Binder)	about 5.0-to about 15.0
	Silicon DC6-2230 (Binder)	up to about 5.0
	Tetrabutylphosphonium Bromide	
	(Conductive salt)	about 0.4-to about 1.2
	Tributyl phosphate	
50	(Plasticizer)	about 1.0-to about 5.0

21

- 5 FC-430 (10% in acetone)
(Surfactant) up to about 1.0
UVITEX OB (Brightener) about 0.1-to about 0.5

10

EXAMPLE 6

This Example illustrates an optimal combination of the ingredients of the jet ink composition of the present invention illustrated in Example 5.

	<u>Materials</u>	<u>Wt. %</u>
15	Acetone	71.65
	Duplicating fluid #5, anhydrous (Solvent)	10.0
20	1-Methyl 2-Pyrrolidone (Solvent)	3.0
	Nitrocellulose RS (10-15 cps, wetted with 30% IPA) (Binder)	10.0
	Silicone DC6-2230	2.0
	Tetrabutylphosphonium Bromide	1.0
25	(Conductive salt)	
	Tributyl phosphate (Plasticizer)	2.0
	FC-430 (10% in acetone)	0.1
	UVITEX OB	0.25
30		<u>100.00</u>

- A jet ink composition was prepared using the ingredients listed above by combining and mixing them until a smooth ink composition was obtained. Duplicating fluid #5 is ethanol denatured with isopropanol and n-propyl acetate.

40

EXAMPLE 7

- This Example illustrates the properties of the marks produced from the inventive ink compositions set forth in Examples 2, 4, and 6. Metal cans from three different suppliers were employed in this study. The cans from supplier 1 were made of aluminum, steel, and tin. The cans from supplier 2 were made of aluminum, and the cans from supplier 3 were made of steel and tin. The cans were subjected to testing under a variety of conditions.

22

The results obtained are set forth below and confirm that
 5 the marks have excellent fading, bleeding and blushing
 resistance.

<u>Cans From Supplier 1</u>		<u>Fading/Bleeding/Blushing*</u>		
		<u>Example 2</u>	<u>Example 4</u>	<u>Example 6</u>
10	Retort 250°F/30min (Cans filled w/98°C water)	No/No/0	No/No/0	No/No/0
	50°C/5min (Cans filled w/98°C water)	No/No/0	No/No/0	No/No/0
	40°C/5min (cans filled w/98°C water)	No/No/0	No/No/0	No/No/0
15	35°C/5min (cans filled w/98°C water)	No/No/0	No/No/0	No/No/0

Coated Cans From Supplier 2

20	Retort (125°C/30mins)	No/No/0	No/No/0	No/No/0
	Dipped in 100°C water/30min	No/No/0		No/No/0
	No/No/0			
	Dipped in 80°C water/30min	No/No/0	No/No/0	No/No/0
	Dipped in 60°C water/30min	No/No/0	No/No/0	No/No/0
25	Dipped in 40°C water/30min	No/No/0	No/No/0	No/No/0

Uncoated Cans From Supplier 2

	Retort (125°C/30mins)	No/No/1	No/No/1	No/No/1
30	Dipped in 100°C water/30min	No/No/0		No/No/0
	No/No/0			
	Dipped in 80°C water/30min	No/No/0	No/No/0	No/No/0
	Dipped in 60°C water/30min	No/No/0	No/No/0	No/No/0
35	Dipped in 40°C water/30min	No/No/0	No/No/0	No/No/0

Cans from Supplier 3

	with red coating			
	(150°F/5min)	No/No/0	No/No/0	No/No/0
40	with black coating			
	(150°F/5min)	No/No/0	No/No/0	No/No/0

*Blushing is reported on a scale of 0-4. A blushing value
 45 of 0 indicates absence of blushing, and a value of 1
 indicates very slight blushing. A mark that exhibits
 extreme blushing will be rated 4.

CLAIMS:

- 5 1. A jet ink composition suitable for printing marks on metal, glass, plastics, rubber, or paper, the composition comprising an ink carrier, a fluorescent colorant, a cellulosic binder resin, and a tetraalkyl ammonium or phosphonium salt.
- 10 2. A jet ink composition as claimed in Claim 1, wherein said composition has (1) a viscosity of from 1.6 to 7.0 centipoises at 25° C; (2) an electrical resistivity of from 50 to 2000 ohm-cm; and (3) a sonic
15 velocity of from 1100 to 1700 meters/second.
3. A jet ink composition as claimed in Claim 1 or 2, wherein said fluorescent colorant comprises 2,2'-(2,5-thiophenediyl)-bis(5-tert-butylbenzoxazole).
- 20 4. A jet ink composition as claimed in any one of claim 1 to 3, wherein said cellulosic binder resin is nitrocellulose.
- 25 5. A jet ink composition as claimed in claim 4, wherein said nitrocellulose has a nitrogen content of about 12% by weight.
6. A jet ink composition as claimed in any one of
30 the preceding claims, wherein said ink carrier comprises acetone, methyl ethyl ketone, methanol or ethanol.
7. A jet ink composition as claimed in any one of the preceding claims, wherein said tetraalkyl ammonium or
35 phosphonium salt is a tetrabutyl ammonium or phosphonium salt.

24

8. A jet ink composition as claimed in any one of
5 the preceding claims further comprising a silicone resin.

9. A jet ink composition as claimed in any one of
the preceding claims, further comprising a high boiling
solvent such as N-methyl pyrrolidone.

10

10. A process of jet printing on metal, glass,
plastic, rubber, or paper substrates, comprising
projecting a stream of ink droplets of a jet ink
composition as claimed in any one of the preceding claims
15 to the surface of said substrates and controlling the
direction of the stream electronically so that the
droplets are caused to form the desired printed mark on
the surface, said marks having blush resistance, bleed
resistance, or fade resistance.

20

25

30

35

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 97/03404

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C09D11/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C09D B41M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 96 04335 A (SUBBARAMAN) 15 February 1996 see page 9, paragraph 1 see page 10, paragraph 1-2 see page 13, line 18-20 see page 17 - page 18 ---	1,4-10
Y	WO 90 01053 A (SIEMENS) 8 February 1990 see claims ---	1,4-10
A	FR 2 369 327 A (M & T CHEMICALS INC.) 26 May 1978 see claims ---	1,2,10
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"S" document member of the same patent family

Date of the actual completion of the international search

12 March 1998

Date of mailing of the international search report

20/03/1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Girard, Y

INTERNATIONAL SEARCH REPORT

Internat J Application No
PCT/GB 97/03404

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 91 17219 A (DR. BECK & CO.) 14 November 1991 see claims & DE 40 13 456 A cited in the application -----	1,10
A	FR 2 325 704 A (AGFA-GEVAERT) 22 April 1977 see claims -----	1,2,10
A	DE 32 41 489 A (DICKFELD DIRK H.) 10 May 1984 see claims -----	3

INTERNATIONAL SEARCH REPORT

Information on patent family members

Internati Application No

PCT/GB 97/03404

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9604335 A	15-02-96	US 5710195 A AU 3625195 A US 5674923 A	20-01-98 04-03-96 07-10-97
WO 9001053 A	08-02-90	DE 3825007 A	25-01-90
FR 2369327 A	26-05-78	AU 2989377 A BE 859820 A BR 7707066 A CS 195341 B DE 2747630 A DK 472877 A GB 1577902 A JP 53055214 A NL 7711755 A SE 7711941 A ZA 7705618 A	26-04-79 15-02-78 18-07-78 31-01-80 27-04-78 27-04-78 29-10-80 19-05-78 28-04-78 27-04-78 29-11-78
WO 9117219 A	14-11-91	DE 4013456 A AT 108815 T DE 59102274 D EP 0526490 A ES 2062783 T JP 7005855 B	31-10-91 15-08-94 25-08-94 10-02-93 16-12-94 25-01-95
FR 2325704 A	22-04-77	DE 2543092 A BE 846472 A GB 1550851 A JP 52041007 A US 4106027 A	07-04-77 23-03-77 22-08-79 30-03-77 08-08-78
DE 3241489 A	10-05-84	NONE	

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☒ FADED TEXT OR DRAWING
- ☒ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☒ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.